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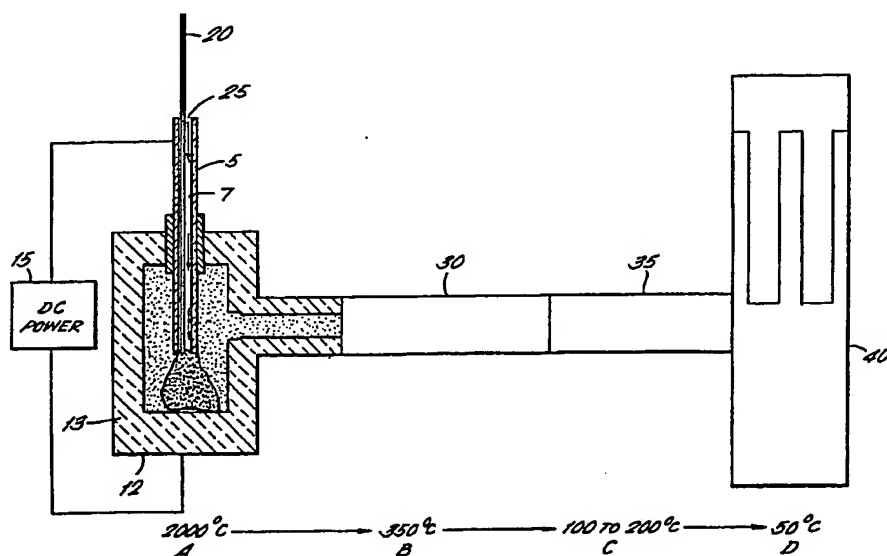
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- (21) International Application Number: PCT/GB01/00553 (74) Agent: **BOULT WADE TENNANT**; Verulam Gardens, 70 Gray's Inn Road, London WC1X 8BT (GB).
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- (71) Applicant (*for all designated States except US*): **TETRONICS LIMITED** [GB/GB]; 5B Lechlade Road, Faringdon, Oxon SN7 9AJ (GB).
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- (75) Inventors/Applicants (*for US only*): **DEEGAN, David, Edward** [GB/GB]; 6 Wright Road, Upper Rissington, Cheltenham, Gloucestershire GL54 2NP (GB). **CHAPMAN, Chris, David** [GB/GB]; Cross Tree Cottage, Kempsford, NR Fairford, Gloucestershire, GL7
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(54) Title: PLASMA ARC REACTOR FOR THE PRODUCTION OF FINE POWDERS



(57) Abstract: A plasma arc reactor and process for producing a powder from a solid feed material, for example aluminium, is provided. The reactor comprises: (a) a first electrode (5), (b) a second electrode (10) which is adapted to be spaced apart from the first electrode by a distance sufficient to achieve a plasma arc therebetween, (c) means for introducing a plasma gas into the space between the first and second electrodes, (d) means for generating a plasma arc in the space between the first and second electrodes, wherein the first electrode has a channel (7) running therethrough, an outlet of the channel exiting into the space between the first and second electrodes, and wherein means are provided for feeding solid material (20) through the channel to exit therefrom via the outlet into the space between the first and second electrodes.



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## PLASMA ARC REACTOR FOR THE PREDUCTION OF FINE POWDERS

5       The present invention relates to an apparatus and  
process for the production of powders. In particular,  
a plasma arc reactor is provided which may be used in  
a plasma evaporation process to produce sub-micron or  
nano-metric (i.e. nano-sized) aluminium powders.

10       Metal and ceramic powders are used in sintering  
processes in metallurgy and in catalysis in the  
chemical industry. The powders may be used in the  
manufacture of structural components, magnetic films,  
chemical coatings, oil additives, propellant additives  
15       and also in explosives.

20       The present invention provides a plasma arc  
reactor for producing a powder from a solid feed  
material, the reactor comprising:

- (a) a first electrode,
- (b) a second electrode which is adapted to be spaced  
25       apart from the first electrode by a distance  
sufficient to achieve a plasma arc therebetween,
- (c) means for introducing a plasma gas into the space  
between the first and second electrodes,
- 30       (d) means for generating a plasma arc in the space  
between the first and second electrodes,

wherein the first electrode has a channel running  
therethrough, an outlet of the channel exiting into  
35       the space between the first and second electrodes, and  
wherein means are provided for feeding solid material

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into and through the channel to exit therefrom via the outlet into the space between the first and second electrodes.

5           The term electrode as used herein is intended to encompass a plasma torch.

10           The first electrode is preferably moveable with respect to the second electrode from a first position at which an arc portion thereof contacts with an arc portion of the second electrode to a second position at which said arc portions are spaced apart from each other by a distance sufficient to achieve a plasma arc therebetween. This is advantageous because contacting  
15           the first and second electrodes assists in starting the plasma arc. It will be appreciated that by the term arc portion is meant those regions or points on the surfaces of the first and second electrodes between which a plasma arc may be generated.

20           The first electrode may preferably take the form of a hollow elongate member whose inner surface defines a closed channel (equivalent to a bore or passageway). The elongate member terminates at an arc  
25           tip, which, in use, will oppose an arc portion of the second electrode. The outlet of the closed channel is disposed at or adjacent to the arc tip. In this case, the first electrode may be in the form of a hollow rod, cylinder or tube. The first electrode may be  
30           formed initially as a hollow object. Alternatively, the first electrode may be formed as a solid object, to subsequently have a bore or passageway formed therein. If the outlet is disposed at the arc tip, then it will be appreciated that the end surface of  
35           the elongate member will define both the arc tip of the electrode and the outlet of the closed channel. the first electrode will typically act as the cathode.

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The second electrode, which acts a counter electrode, may take any appropriate form to enable a plasma arc to be generated between it and the first electrode. The second electrode may simply have a substantially planar arc portion. For example, the second electrode may be disposed as a planar substrate on the bottom wall of the plasma reactor.

The arc portions of the first and/or second electrodes will generally be formed from carbon, preferably graphite.

The plasma reactor may be provided in the form of a graphite lined vessel or a graphite crucible, in which a portion thereof acts as the second electrode. Accordingly, the second electrode may be integrally formed with the reactor vessel.

In a preferred embodiment, part or all of the interior surface of the plasma arc reaction chamber constitutes the second electrode. The chamber may be a graphite reaction chamber or a graphite lined reaction chamber.

It is also preferable to make the second electrode the anode so that, in use, metal ions are electrostatically repelled from it.

Neither the first electrode nor the second electrode needs to be earthed.

The plasma arc reactor advantageously further comprises cooling means for cooling and condensing solid material which has been vaporised in the plasma arc generated between the first and second electrodes. The cooling means preferably comprises a source of a cooling gas.

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The second electrode preferably comprises a graphite vessel having a surface adapted to direct vaporised material downstream to a cooling zone to be cooled, in use, by a cooling gas.

5

A collection zone may be provided downstream of the cooling zone for collecting a powder of the condensed vaporised material. The collection zone may comprise a filter cloth which separates the powder particulate from the gas stream. The filter cloth is preferably mounted on an earthed cage to prevent electrostatic charge build up. The powder may then be collected from the filter cloth, preferably in a controlled atmosphere zone. The resulting powder product is preferably then sealed, in inert gas, in a container at a pressure above atmospheric pressure.

The channel in the first electrode is advantageously adapted to additionally introduce the plasma gas into the space between the first and second electrodes. Thus, the solid feed material and plasma gas may travel through a common channel and exit the electrode via a common outlet into the space between the first and second electrodes.

25

The means for generating a plasma arc in the space between the first and second electrodes will generally comprise a DC or AC power source.

If desired, one or more additional electrodes, also having a material feed channel therein, may be used to enable different materials to be co-fed into a single plasma reactor. A common counter electrode may be used or, alternatively, separate counter electrodes may be provided, each opposing an electrode with a channel therein. Common or separate power supplies may be used, although separate power supplies are

30  
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- 5 -

preferred since this allows different evaporation rates for different materials.

5       The apparatus according to the present invention may operate without using any water-cooled elements inside the plasma reactor and may also allow replenishment of solid feed material without stopping the reactor. Water cooling may result in thermal shock and material fracture. There may also be  
10       undesirable reactions between water vapour and the material being processed.

      The apparatus according to the present invention may further comprise means for conveying solid feed  
15       material to the first electrode. If the solid feed material is in the form of a wire, then the apparatus preferably comprises a supply of wire. For example, the apparatus may comprise a container or holder for the wire, preferably a coil or reel. Means are also  
20       preferably provided for conveying the wire from the supply of wire to the first electrode, where the wire is fed into the channel. this may be achieved, for example, by the use of an electric motor.

25       The present invention also provides a process for producing a powder from a solid feed material, which process comprises:

30       (i) providing a plasma arc reactor as herein described,

      (ii) introducing a plasma gas into the space between the first and second electrodes,

35       (iii) generating a plasma arc in the space between the first and second electrodes,

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(iv) feeding solid material through the channel to exit via the outlet thereof into the plasma arc, whereby the solid feed material is vaporised,

5 (v) cooling the vaporised material to condense a powder, and

(vi) collecting the powder.

10 The process according to the present invention may be considered a gas/vapour phase condensation process. In such a process, a plasma is generated to vaporise the solid feed material and material fragmentation occurs in the vapour phase. The vapour  
15 is subsequently cooled and transforms to a solid phase particulate.

The solid feed material will generally comprise or consist of a metal, for example aluminium, nickel  
20 or tungsten, including alloys that include one or more of these metals. Aluminium and aluminium alloys are preferred. The solid feed material may be provided in any suitable form which allows it to be fed into and through the channel to exit therefrom into the space  
25 between the electrodes. For example, the material may be in the form of a wire, fibres and/or a particulate. The solid feed material does not need to be provided in a secondary supporting phase, such as a liquid carrier.

30

The solid feed material is preferably provided in the form of a continuous wire. This is advantageous because it has been found that providing the solid feed material in the form of a wire assists in  
35 delivering the material to the plasma zone and into the plasma core.



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The plasma gas will generally comprise or consist of an inert gas, for example helium and/or argon.

5       The plasma gas is advantageously injected into the channel in the first electrode to exit therefrom into the space between the first and second electrodes. In this case, the plasma gas and solid material preferably exit the first electrode via a common outlet. The plasma gas and solid material may  
10       be fed into the channel in the first electrode via a common inlet or, alternatively, via separate inlets. During operation, the plasma gas and solid material will be co-fed into the channel.

15       The volume flow rate of the plasma gas is preferably monitored to optimise material-to-plasma heat transfer characteristics and to encourage the material to partition towards the vapour phase.

20       At least some cooling of the vaporised material may be achieved using an inert gas stream, for example argon and/or helium. Alternatively, or in combination with the use of an inert gas, a reactive gas stream may be used. The use of a reactive gas enables oxide  
25       and nitride powders to be produced. For example, using air to cool the vaporised material can result in the production of oxide powders, such as aluminium oxide powders. Similarly, using a reactive gas comprising, for example, ammonia can result in the  
30       production of nitride powders, such as aluminium nitride powders. The cooling gas may be recycled via water-cooled conditioning chamber.

35       The surface of the powder may be oxidised using a passivating gas stream. This is particularly advantageous when the material is aluminium or aluminium-based. The passivating gas may comprise an

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oxygen-containing gas, and a particularly preferred gas comprises from 95 to 99 vol.% of an inert gas, such as helium and/or argon, and from 1 to 5 vol.% of oxygen, more preferably approximately 98 vol.% of the inert gas(es) and approximately 2 vol.% of oxygen.

Such a gas mixture has been found to produce particularly good results for aluminium and aluminium-based materials. The passivating gases are preferably premixed to avoid local gas phase enrichment and the possibility of explosions. The (inert) cooling gas may be recycled and subsequently diluted with oxygen at a rate of typically 1 NM<sup>3</sup>/hour to provide the passivating gas stream. The aluminium acts as a getter for the oxygen and reacts with it with the result that the partial pressure inside the chamber falls. If the pressure in the chamber is monitored, then a subsequent rise in the partial pressure indicates that the surface of the aluminium powder has been substantially fully passivated. The reactivity of some ultra-fine powders presents an operational risk if there is a likely-hood of contact with, for example, water and/or air. The passivation stage renders the powdered material more suitable for transporting.

For aluminium for certain applications, it is preferable that substantially no oxidation occurs in the plasma. It also preferable that cooling of the vaporised material is achieved using an inert gas stream, for example argon and/or helium. Accordingly, the passivation stage preferably occurs only after the powder has been cooled. In a preferred embodiment, the solid feed material, for example aluminium wire, is fed to the core of the plasma where it is vaporised. The metal vapour is then conveyed to a separate quenching region where it is quenched in an inert gas stream and transforms to a solidified

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powder. This solid powder is then exposed to oxygen under low temperature oxidation conditions so that the oxide grows to a limiting thickness and then self regulates, i.e. the oxide inhibits further oxidation.

5 This oxygen exposure/reaction process occurs away from the plasma core.

The process according to the present invention may be used to produce a powdered material, such as aluminium, substantially all of the particles of which  
10 having a diameter of less than 200 nm. Preferably the average particle diameter lies in the range of from 50 to 150 nm, more preferably from 80 to 120 nm, still more preferably from 90 to 110 nm.

15 Specific surface area analysis has shown that the process according to the present invention may be used to produce a powdered material, such as aluminium, which has a specific surface area typically in the  
20 range of from 15 to 40 m<sup>2</sup>g<sup>-1</sup>, more typically in the range of from 25 to 30 m<sup>2</sup>g<sup>-1</sup>.

It will be appreciated that the processing conditions, such as material and gas feed rates,  
25 temperature and pressure, will need to be tailored to the particular material to be processed and the desired size of the particles in the final powder.

Preferably, part or all of the interior surface  
30 of the reaction vessel constitutes the second electrode. The second electrode is preferably the anode and the first electrode is preferably the cathode. For certain applications, the first and/or the second electrodes are preferably formed from a  
35 material that does not react with the feed material at the temperature involved.

- 10 -

Both the first and second electrodes are preferably formed of a carbon material, more preferably graphite. Accordingly, the reaction vessel may be a graphite reaction chamber or a graphite lined reaction chamber, which constitutes the second electrode.

It is generally preferable to pre-heat the reactor before vaporising the solid feed material. The reactor may be preheated to a temperature of up to typically 2500°C, more typically from 500°C to 2500°C. For an aluminium feed material, the reactor is preferably preheated to a temperature of from 2000°C to 2500°C, more preferably from 2200°C to 2500°C, still more preferably from 2300°C to 2500°C. Pre-heating may be achieved by any suitable means, although it is preferably achieved using the plasma arc. Preferably, substantially all of the interior of the reaction vessel is pre-heated.

20

The rate at which the solid feed material is fed into the channel in the first electrode will affect the product yield and powder size. When using aluminium wire, a feed rate of from 1 to 5 kg/hour has been used, more typically approximately 2 kg/hour. The aluminium wire is typically 1 to 10 mm gauge, more typically 1 to 5 mm.

The inert plasma gas, for example helium, may also be injected through the channel in the first electrode at a rate of from 2.4 to 6 Nm<sup>3</sup>/h, more typically approximately 3 Nm<sup>3</sup>/hour.

If a DC power supply is used to generate the plasma arc, then the DC amperage will generally be set at a value in the range of from 400 to 800 A. Typical

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DC Electrical characteristics are of the order of 800 A and between 30 to 40 V with a plasma arc column length of between 60 mm and 70 mm.

5           The process and the plasma arc reactor according to the present invention are typically operated at above atmospheric pressure, more typically in excess of 750 mm of water above atmospheric pressure. This prevents or assists in preventing the ingress of  
10       atmospheric oxygen into the plasma zone, which may result in an undesirable chemical reaction. When the feed material is aluminium, it is preferable to operate the plasma arc reactor above atmospheric pressure, typically up to 45 inWG (inches water  
15       gauge), more typically from 15 to 35 inWG. Operating at a pressure above atmospheric pressure also has the advantage that it results in a higher yield of particulate material.

20           If a cooling gas, preferably an inert gas such as argon or helium is used to cool and condense the vaporised material, a flow rate of from 60 to 120 Nm<sup>3</sup>/h has been found to result in an aluminium powder in which most, if not substantially all, of the  
25       particles have a diameter of less than 200 nm in diameter (more typically  $\leq$  100 nm). After cooling, the gas and particulate temperature will typically be from 300 to 350°C.

30           For an aluminium feed material, the process according to the present invention may be used to produce a powdered material having a composition based on a mixture of aluminium metal and aluminium oxide. This is thought to arise with the oxygen addition made  
35       to the material during processing under low temperature oxidation conditions. Accordingly, the present invention also provides a particulate material

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comprising particles having a core comprising or  
consisting essentially of aluminium and a surface  
layer comprising or consisting essentially of  
aluminium oxide, which particulate material is  
5 obtainable by a process as herein described.

Substantially only the surface of the particles  
oxidise and surface specific analysis has shown that  
the oxide component of the powder is associated  
10 generally with the surface and the oxide layer is  
typically less than approximately 10 nm in thickness,  
more typically less than approximately 5 nm in  
thickness. Hence, such a material can be described as  
discreetly encapsulated. Substantially all of the  
15 particles of the oxide coated aluminium have a  
diameter of less than 200 nm and the average particle  
diameter will typically lie in the range of from 50 to  
150 nm, more typically from 80 to 120 nm, still more  
typically from 90 to 110 nm. The specific surface  
20 area of the oxide coated aluminium particles will  
typically be in the range of from 15 to 40 m<sup>2</sup>g<sup>-1</sup>, more  
typically in the range of from 25 to 30 m<sup>2</sup>g<sup>-1</sup>.

Examination of the particulate using TEM and  
25 electron diffraction indicates that the aluminium  
particles are essentially single crystal, i.e. mono-  
crystalline.

The present invention will now be described  
30 further, by way of example, with reference to the  
accompanying drawings in which:

Figure 1 shows one embodiment of an electrode  
configuration which may be used in a plasma arc  
35 reactor according to the present invention;

Figure 2 provides a flow diagram of a process

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according to the present invention;

Figures 3 (a) and (b) are secondary electron micrographs of aluminium powders made by the process according to the present application (magnification: x 100,000 (a) and x 200,000 (b));

Figure 4 is a graph showing the variation of specific surface area of an ideal nanometric aluminium powder with particle diameter;

Figure 5 is a graph showing the variation of oxide content of an ideal nanometric aluminium powder with particle diameter;

Figure 6 is a graph showing primary (1<sup>st</sup> heat) DSC analysis for an aluminium sample;

Figure 7 is a graph showing secondary (2<sup>nd</sup> heat) DSC analysis for an aluminium sample; and

Figure 8 is a survey spectrum of nanometric Al powder analysed by XPS.

In Figure 1, a first electrode 5 is provided in the form of a cylindrical graphite rod which terminates at an arc tip 6. If desired, the upper portion of the graphite electrode 5 may be replaced with copper. The electrode 5 has a central bore formed therein which extends along the length of the electrode 5. The surface of the bore defines a closed channel 7 (or passageway) having an inlet 8 at one end and an outlet 9 disposed at the arc tip 6.

A second counter electrode 10 is provided as part of a graphite-lined reactor vessel (13) (see Figures 1

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and 2). Only an arc portion 11 on the interior surface of the bottom wall 12 of the vessel 13 is shown in Figure 1. The whole of the vessel 13 is shown in Figure 2 and it can be seen that the counter electrode forms an integral part of the reactor vessel 13. The arc portion 11 of the second electrode 10 opposes the arc tip 6 of the first electrode 5.

The first 5 and second 10 electrodes are connected to a DC power supply 15. The first electrode 5 is the cathode and the second electrode is the anode 10, although it will be appreciated that the polarities may be reversed.

The first electrode 5 is moveable with respect to the second electrode 10 and hence may be lowered to contact at the arc tip 6 thereof with the arc portion 11 of the second electrode 10 to complete the electrical circuit. The DC amperage from power supply 15 will generally be set at a value from 400 to 800 A. By raising the first electrode 5, a DC plasma arc can be established between the arc tip 6 of the first electrode 5 and the arc portion 11 of the second electrode 10.

A solid feed material, for example aluminium wire 20, can be fed into the inlet 8, to pass down the channel 7, out the outlet 9 and into the space between the arc tip 6 of the first electrode 5 and the arc portion 11 of the second electrode 10. An inert plasma gas 25, such as argon and/or helium, may similarly be injected through the channel 7, via the inlet 8, to exit the first electrode 5 at outlet 9. Accordingly, both the aluminium wire 20 and the plasma gas 25 may enter the first electrode 5 via a common inlet 8 and exit the electrode 5 via a common outlet 9 at the arc tip 6.



- 15 -

The wire 20 may be stored by conventional means on a coil or reel and fed by a multi-speed motor into inlet 8. The plasma gas 25 may be stored by conventional means in a gas tank, and controlled injection into the inlet may be achieved by the use of a valve. Accordingly, the feed rates of both the wire and the plasma gas may be controlled.

In use, the graphite-lined vessel 10 is preheated to a temperature of at least about 2000°C (typically approximately 2200°C to 2300°C) using the plasma arc. This entails injecting an inert plasma gas 25 through channel 7 in the first electrode 5 and switching on the power supply 15.

The reactor is typically operated in excess of 750 mm of water above atmospheric pressure.

Once the reactor has been pre-heated, aluminium wire 20 is then fed into the inlet 8 of channel 7 in the first electrode 5 at a rate of typically 2 kg/hour. Inert plasma gas is also injected through channel 7, typically at a rate of from 2.4 and 6 Nm<sup>3</sup>/h, more typically approximately 3 Nm<sup>3</sup>/hour.

Typical DC electrical characteristics are of the order of 800 A and from 30 to 40 V with a plasma arc column length of from 60 mm and 70 mm.

In this manner, the aluminium wire 20 is vaporised in the hot plasma gas (step A in Figure 2). The wire 20 and plasma gas 25 are continually fed into the channel 7 of the first electrode 7 as the wire 20 is vaporised in the plasma arc. Eventually a steady-state will be achieved. It will be appreciated that the feed rates of the wire 20 and/or gas 25 may be adjusted during processing.

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The vaporised aluminium and plasma hot gas exits the reactor vessel under the influence of the gas being injected through the channel 7 in the first electrode 5. The vaporised aluminium is then quenched in a cooling zone 30 using an inert cooling gas stream, such as argon or helium, to condense a sub-micron powder of aluminium (step B in Figure 2). The flow rate of the cooling gas stream is typically from 60 to 120 Nm<sup>3</sup>/h, and the particles of the aluminium powder are typically  $\leq 200$  nm in diameter (more typically  $\leq 100$  nm). After the inert gas quench, the gas and particulate temperature is typically from 300 to 350°C.

If desired, a passivation step may next be carried out in a passivation zone 35 downstream of the cooling zone 30 (step c in Figure 2). This may be achieved in a number of ways. The cooling gas may be recycled to a water-cooled conditioning chamber for further cooling, and then injected back into the apparatus, together with up to 5 vol.% of oxygen to contact with the powder. Typically, the oxygen is introduced at a rate of approximately 1 Nm<sup>3</sup>/h. Alternatively, a separate source of the passivation gas may be used. The temperature during the passivation step is typically in the range of from 100 to 200°C.

After the passivation step, the powder particulate and gas stream pass to a collection zone 40 which contains a filter cloth (not shown) to separate the particulate from the gas (see step D in Figure 2). The filter cloth is preferably mounted on an earthed cage to prevent electrostatic charge build up. The gas may be recycled.

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The powder may then be collected from the filter cloth, preferably in a controlled atmosphere zone. The resulting powder product is preferably then sealed, in inert gas, in a container at a pressure  
5 above atmospheric pressure.

If desired, one or more additional electrodes having a channel therein may be used to co-feed different metals into a single plasma vessel to  
10 produce, for example, alloy powders, sub-micron and nano-sized mixtures, oxides and nitrides. A common counter electrode may be used or, alternatively, separate counter electrodes may be provided, each opposing an electrode with a channel therein. Common  
15 or separate power supplies may be used, although separate power supplies are preferred since this allows for different evaporation rates for different metals.

#### 20 Example

This example relates to the production of an nano-metric aluminium powder using atmospheric DC plasma technology, which is a clean, controllable and  
25 directional heat source. Aluminium powders may be used in sintering processes in metallurgy and in catalysis in the chemical industry. The powders may be used in the manufacture of structural components, magnetic films, chemical coatings, oil additives,  
30 propellant additives and also in explosives.

The process utilises the mechanism of gas phase condensation. The process offers the advantage of high throughput (Kg/hr) under mixed inert gas process  
35 conditions, followed by controllable material passivation during pneumatic conveyance and dispersion above atmospheric pressure. The material is produced,

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cooled, passivated (i.e. surface oxidised under low temperature conditions), collected and packaged in a highly monitored and automated manner.

5           The original feed wire (precursor) used in the process is a wrought alloy with the designation 1050A, ASTM = ER1100, DIN = S-AL 9915. This wire has a nominal composition of 99.5 wt% Al, the main impurities are Si and Fe at a maximum of 0.25 wt% and  
10           0.40 wt% respectively.

          The aluminium and aluminium oxide content cannot be determined directly, so a quantitative elemental analysis of major powder components was undertaken.  
15           The calculation assumed all oxygen was combined as aluminium oxide, having the stoichiometry  $Al_2O_3$ . A pre-calibrated Leco TC436 oxygen and nitrogen analyser was used to determine oxygen content. A pre-calibrated Leco CS344 carbon and sulphur analyser was  
20           used for carbon analysis. Energy dispersive X-ray fluorescence spectroscopy (EDXRF) was used to check powder for high levels of contamination. An ARL 3410 inductively coupled plasma atomic emission spectrometer (ICPAES) was used to quantitatively  
25           analyse the solutions for high level of contaminant identified by EDXRF.

          The EDXRF analysis showed significant levels of calcium, although other contaminants were found at  
30           very low levels, for example Fe, Na, Zn and Ga. Hence the quantitative analysis focussed on O, C and Ca. The Al content can be assumed to make up the majority of the remaining powder after subtraction of the alumina, calcium and carbon content. The carbon  
35           content was assumed as elemental due to the insoluble residue left in the container during ICPAES analysis. The analysis results are shown in Table 1

Table 1: Combined Material Analysis Results

Specimen ID	C wt%	Ca wt%	O wt%	Calculated wt% Al <sub>2</sub> O <sub>3</sub>	Calculated wt% Al
6AL	2.48	0.17	14.9		
6AL	2.41	0.17	15.4		
6AL			16.3		
Mean	2.44	0.17	15.5	33	64.4

Oxygen is purposely added to the system under low temperature oxidation conditions

10

Aluminium powder samples have been examined by scanning electron microscopy (SEM) using a Leica Cambridge S360 instrument. Electron micro-graphs were prepared to show the size and shape of the particles. Quantitative energy dispersive (ED) X-ray analysis was carried out to determine the elements present in the sample using a PGT IMIX X-ray analysis system attached to the SEM.

20

Secondary electron detection was used to give topographic textured images of the aluminium powder particulate and associated agglomerates. At low magnification (x 350 magnification) the powder product was observed to have agglomerated. The size of the agglomerates ranged from less than 5 µm to more than 200 µm. At higher magnification (x 20,000 and 50,000 magnification) the individual particles could be imaged. Their size (i.e. largest dimension) was observed to be approximately 100 nm ± 50 nm, however the particles still appeared to be clumped together. These agglomerates were determined to be made up of these finer particles. The shape of the particles seemed to be irregular either spherical or oval. The shape of the individual particles and the process of agglomeration are thought to occur to minimise the excess surface free energy associated with such a

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finely divided material. Two secondary electron micrographs are shown in Figures 3 (a) and (b).

5 Transmission electron microscopy (TEM) has shown that the particles typically have a generally spherical morphology. Corresponding electron diffraction work indicates that the particles are typically essentially mono-crystalline.

10 The specific surface area (SSA) was determined by nitrogen absorption, using the continuous flow method, described in BS 4359 Part 1. The SSA was shown to lie in the range of from 25 to 30 m<sup>2</sup>g<sup>-1</sup>. Figure 4 shows the variation of specific surface area with particle  
15 size for an ideal chemically pure, spherical aluminium powder. Figure 4 indicates that a mean particle size of 90 nm is consistent with a specific surface area of from 25 to 30 m<sup>2</sup>g<sup>-1</sup>. So the SEM images show consistency with the SSA analysis.

20

The fraction of oxide in the powder will shift unfavourably as the powder particulate size becomes smaller, i.e. the proportion of oxide will increase relative to that of the metal. This trend is  
25 graphically represented in Figure 5, here a uniform oxide layer of 4.5 nm thickness is assumed. This represents the diffusion limited adherent, coherent and uniform oxide film associated with aluminium material exposed to an oxygen rich atmosphere under  
30 low temperature conditions.

Again the compositional analysis indicated an oxide content of 33 wt%, this gives rise to an implied particle size of from 90 to 100 nm. This again being  
35 consistent with the SSA analysis and SEM images.

Thermal analysis was carried out using a

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Differential Scanning Calorimetry (DSC). The instrument was initially checked for temperature and energy calibration using a traceable indium standard. The sample was heated to 750°C at a heating rate of 10°C min<sup>-1</sup> under air flowing at 5 ml min<sup>-1</sup>. The DSC spectrum shows an exothermic (energy is released) peak with an extrapolated onset temperature of 538°C. The peak range is from 538 to 620°C, with the peak maximum at 590°C. After initial heating the sample was cooled and reheated under the same conditions and no exotherm was observed. This indicated a complete and irreversible chemical reaction, i.e. oxidation of aluminium. This is graphically represented in the Figures 6 and 7.

The technique of X-ray Photoelectron Spectroscopy (XPS) is surface sensitive and the outermost 2 to 3 layers of a material (i.e. the top 1 nm) is typically analysed. This gives both compositional and chemical information. For example, XPS can distinguish between Al as a bulk metal and Al associated with an oxide Al<sub>2</sub>O<sub>3</sub>. The survey spectrum showed the presence of the following species, Table 2:

**Table 2: Peak Component Assignment**

284.7	C1s	Environmental Carbon Contamination
72.2	Al2p	Metal
74.2	Al2p	Al <sub>2</sub> O <sub>3</sub>
531.6	O1s	Al <sub>2</sub> O <sub>3</sub>
1071.5	Na1s	Na <sub>2</sub> CO <sub>3</sub>
2061.3	Na Auger Parameter	Na <sub>2</sub> CO <sub>3</sub>
289.4	C1s	Na <sub>2</sub> CO <sub>3</sub>

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The survey spectrum is provided in Figure 8 and shows the presence of carbon (19 atomic %), oxygen (50 atomic %), aluminium (27 atomic %), nitrogen (0.6 atomic %), sodium (3.3 atomic %) and calcium (0.7 atomic %). These values were calculated using published sensitivity factors (Briggs and Seah 1990). Detailed spectra were taken off the main peak to provide chemical information in the form of binding energies, we did not take into account factors such as morphology, topography and heterogeneity. The carbon peak was used to calibrate the spectrum, i.e. adventitious carbon contamination (environmental contamination), binding energy 287.4 eV. The compositional information relates to the outer 2 to 3 layers of the particulate material and, accordingly, should not be interpreted as the overall bulk composition of the material.

Al2p peak showed two superimposed components due to the metal and the native oxide with binding energies of 72.1 eV and 74.1 eV respectively. The fact that the aluminium metal associated with the interior of the particulate could be detected, i.e. the substrate metal, through the oxide indicates a thin overlayer of less than 2 to 3 monon-layers (Crystallography: Corundum has a rhombohedral crystal system where  $a = b = c = 12.98 \text{ \AA}$ ). The carbon peak was observed to be made up of two components, i.e. environmental contamination and carbide. The carbon could not be categorically associated with any one of the metal species detected. The sodium is probably present as carbonate ( $\text{Na}_2\text{CO}_3$ ).

It is possible to estimate the thickness of the monolayer using the De Beers - Lambert equations and associated assumptions.



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De Beers - Lambert Equation, Version 1

$$I^{ox} = I_o^{ox} [1 - \exp(-d/\lambda \sin\theta)] \quad (1)$$

5 De Beers - Lambert Equation, Version 2

$$I^{element} = I_o^{element} [\exp(-d/\lambda \sin\theta)] \quad (2)$$

10 where  $\lambda$  is the inelastic electron mean  
free path  $\lambda = 0.05(KE)^{0.5} \text{ nm} =$   
 $0.05(1486.6 - 73)^{0.5} = 1.8799 \text{ nm}$  (KE =  
ejected electron kinetic energy)

15 If the oxide is native to the metallic material  
element then  $I_o$  and  $\lambda$  are approximately the same.  
Hence, by dividing equation 1 by equation 2, an  
equation relating the relative Al signal intensities  
to oxide layer thickness may be obtained:

$$20 \quad I^{ox} / I^{element} = \exp(d/\lambda \sin\theta) - 1 \quad (3)$$

The assumptions associated with the use of this  
equation are as follows:

- 25 (i) the surfaces are flat;  
(ii) the oxide layer is uniform in thickness;  
(iii) the layer is continuous; and  
(iv) the surfaces are planar.

30 The outcome of this calculation is that the oxide  
layer is approximately 2 to 3 nm in thickness, which  
is consistent with the compositional analysis, SSA  
analysis and SEM images. The variability being  
associated with the inaccuracy of the assumptions made  
35 in calculation. This calculation is very inaccurate,  
however the technique will only analyse the uppermost

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nm of sample as a maximum depth. This means that as a parent metal signal is observed in the survey spectrum, the oxide thickness must be less than 5 nm, this being a definite statement associated with the nature of the characterising radiation.

The particulate material according to the present invention has the following characteristics:

1. In composition the material is observed to be a mixture of aluminium metal and aluminium oxide, which is consistent with the oxygen addition made to the material during processing under low temperature oxidation conditions, i.e. substantially only the surface oxidises.
2. Imaging indicates that the material is formed with a fine spherical particulate morphology of from 70 to 130 nm in average particle diameter, (more typically from 80 to 120 nm, still more typically approximately 100 nm). This justifies the classification as a nanomaterial.
3. The particles are agglomerated by which is meant an assembly of particles held together by weak forces that can be overcome by suitable means, for example sonication.
4. Specific surface area analysis has shown that the material has a specific surface area typically in the range of from 15 to 40 m<sup>2</sup>g<sup>-1</sup>, more typically in the range of from 25 to 30 m<sup>2</sup>g<sup>-1</sup>. This correlates typically to a particle size of from 75 to 95 nm.
5. Thermal analysis has shown complete and irreversible chemical reaction takes place in air

- 25 -

at 550 to 650°C. This being consistent with thermally driven oxidation.

5       6.    Surface specific analysis has shown that the  
oxide component of the powder is associated with  
the surface and the layer is less than  
approximately 5 nm in thickness. Hence the  
material can be described as discreetly  
encapsulated.

10       The apparatus and process according to the  
present invention provide a simplified technique for  
the production and collection of sub-micron and nano-  
metric powders. In a preferred embodiment, a  
15   transferred plasma arc is established between the arc  
tip of an elongate graphite electrode and a counter  
electrode formed as part of a graphite reactor  
crucible.

20       The apparatus according to the present invention  
may operate without using any water-cooled elements  
inside the plasma reactor and allows replenishment of  
feed material without stopping the reactor.

25       The reactivity of sub-micron and nano-metric  
metals, such as aluminium, presents an operational  
risk if there is a likely-hood of contact with water,  
reactive liquids, or reactive gases such as air and  
oxygen. The passivation stage described herein  
30   renders the powdered material more suitable for  
transporting.

35

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**CLAIMS:**

1. A plasma arc reactor for producing a powder from a solid feed material, the reactor comprising:

5

(a) a first electrode,

10

(b) a second electrode which is adapted to be spaced apart from the first electrode by a distance sufficient to achieve a plasma arc therebetween,

(c) means for introducing a plasma gas into the space between the first and second electrodes,

15

(d) means for generating a plasma arc in the space between the first and second electrodes,

20

wherein the first electrode has a channel running therethrough, an outlet of the channel exiting into the space between the first and second electrodes, and wherein means are provided for feeding solid material through the channel to exit therefrom via the outlet into the space between the first and second electrodes.

25

2. A plasma arc reactor as claimed in claim 1, wherein the first electrode is moveable with respect to the second electrode from a first position at which an arc portion thereof contacts with an arc portion of the second electrode to a second position at which said arc portions are spaced apart from each other by a distance sufficient to achieve a plasma arc therebetween.

30

35

3. A plasma arc reactor as claimed in claim 1 or claim 2, wherein the first electrode is a hollow elongate member whose inner surface defines a closed

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channel, the elongate member terminating at an arc tip which opposes the second electrode, wherein the outlet of the closed channel is disposed at or adjacent to the arc tip.

5

4. A plasma arc reactor as claimed in any one of the preceding claims, wherein arc portions of the first and/or second electrodes is/are formed from graphite.

10

5. A plasma arc reactor as claimed in any one of the preceding claims, further comprising cooling means for cooling and condensing solid feed material which, in use, has been vaporised in the plasma arc between the first and second electrodes.

15

6. A plasma arc reactor as claimed in claim 5, wherein the cooling means comprises a source of a cooling gas.

20

7. A plasma arc reactor as claimed in claim 6, wherein the second electrode comprises a graphite vessel having a surface adapted to direct vaporised solid material downstream to a cooling zone to be cooled, in use, by the cooling gas.

25

8. A plasma arc reactor as claimed in any one of the preceding claims, further comprising a collection zone for collecting powdered material.

30

9. A plasma arc reactor as claimed in any one of the preceding claims, wherein the channel in the first electrode is also adapted to introduce the plasma gas into the space between the first and second electrodes.

35

10. A plasma arc reactor as claimed in any one

- 28 -

of the preceding claims, wherein the means for generating a plasma arc in the space between the first and second electrodes comprises a DC or AC power source.

5

11. A plasma arc reactor as claimed in any one of the preceding claims, further comprising means for conveying solid feed material to the first electrode.

10

12. A plasma arc reactor as claimed in claim 11, wherein said means comprising means for conveying solid feed material in the form of a wire to the first electrode.

15

13. A plasma arc reactor as claimed in claim 12, further comprising a container or holder for a solid feed material in the form of a wire and preferably means for conveying wire from the container or holder to the first electrode.

20

14. A process for producing a powder from a solid feed material, which process comprises:

(i) providing a plasma arc reactor as defined in any one of the preceding claims,

25

(ii) introducing a plasma gas into the space between the first and second electrodes,

30

(iii) generating a plasma arc in the space between the first and second electrodes,

(iv) feeding solid material through the channel to exit via the outlet thereof into the plasma arc, whereby the solid feed material is vaporised,

35

(v) cooling the vaporised material to condense a

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powder, and

(vi) collecting the powder.

5           15. A process as claimed in claim 14, wherein  
the solid feed material comprises or consists of a  
metal or alloy.

10           16. A process as claimed in claim 15, wherein  
the solid feed material is aluminium or an alloy  
thereof.

15           17. A process as claimed in any one of claims 14  
to 16, wherein the solid feed material is in the form  
of a wire, fibres and/or a particulate.

20           18. A process as claimed in any one of claims 14  
to 17, wherein the plasma gas comprises or consists of  
an inert gas.

            19. A process as claimed in claim 18, wherein  
the plasma gas comprises or consists of helium and/or  
argon.

25           20. A process as claimed in any one of claims 14  
to 19, wherein the plasma gas is injected through the  
channel of the first electrode to exit therefrom into  
the space between the first and second electrodes.

30           21. A process as claimed in claim 20, wherein  
the plasma gas and solid feed material exit the first  
electrode via a common outlet.

35           22. A process as claimed in claim 20 or claim  
21, wherein the plasma gas and solid feed material  
enter the channel in the first electrode via a common  
inlet.

- 30 -

23. A process as claimed in any one of claims 14 to 22, wherein at least some cooling of the vaporised material is achieved using an inert gas stream.

5        24. A process as claimed in any one of claims 14 to 23, wherein at least some cooling of the vaporised material is achieved using a reactive gas stream.

10       25. A process as claimed in any one of claims 14 to 24, wherein the surface of the powder is oxidised using a passivating gas stream.

15       26. A process as claimed in claim 25, wherein the passivating gas comprises an oxygen-containing gas.

20       27. A process as claimed in claim 26, wherein the oxygen-containing gas comprises from 95 to 99 vol.% of an inert gas and from 1 to 5 vol.% of oxygen.

25       28. A process as claimed in claim 27, wherein the oxygen-containing gas comprises approximately 98 vol.% of an inert gas and approximately 2 vol.% of oxygen.

30       29. A process as claimed in any one of claims 14 to 28, wherein the powder comprises particles substantially all of which have a diameter of less than 200 nm.

35       30. A process for producing a passivated aluminium powder from a solid feed material of aluminium wire, which process comprises:

(A) providing a plasma arc reactor,

(B) supplying inert gas to the reactor and



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generating an inert gas plasma in the reactor,

(C) feeding aluminium wire into the inert gas plasma, whereby the aluminium is vaporised,

5

(D) cooling the vaporised aluminium with an inert gas to condense a powder of aluminium, and

(E) oxidising the surface of the powder of aluminium with a passivating gas.

10

31. A process as claimed in claim 30, wherein the reactor is as defined in any one of claims 1 to 13.

15

32. A process as claimed in any one of claims 14 to 31, wherein the reactor is pre-heated to a temperature of from 2000 to 2500°C, preferably 2200 to 2300°C prior to vaporising the solid feed material.

20

33. A process as claimed in any one of claims 14 to 33, wherein the pressure in the reactor is maintained at a level above atmospheric pressure.

25

34. A particulate material comprising particles having a core comprising or consisting essentially of aluminium and a surface layer comprising or consisting essentially of aluminium oxide, which particulate material is obtainable by a process as claimed in any one of claims 16 to 33.

30

35. A particulate material as claimed in claim 34, wherein the aluminium oxide surface layer has a thickness of  $\leq 10$  nm, preferably  $\leq 5$  nm, more preferably  $\leq 3$  nm.

35

36. A particulate material as claimed in claim

- 32 -

34 or claim 35, wherein substantially all of the particles have a diameter of  $\leq 200$  nm.

5           37. A particulate material as claimed in any one of claims 34 to 36, wherein the average particle diameter lies in the range of from 50 to 150 nm, more preferably from 70 to 130 nm, still more preferably from 80 to 120 nm.

10           38. A particulate material as claimed in any one of claims 34 to 37, wherein the particulate material has a specific surface area in the range of from 15 to 40 m<sup>2</sup>g<sup>-1</sup>, preferably from 25 to 30 m<sup>2</sup>g<sup>-1</sup>.

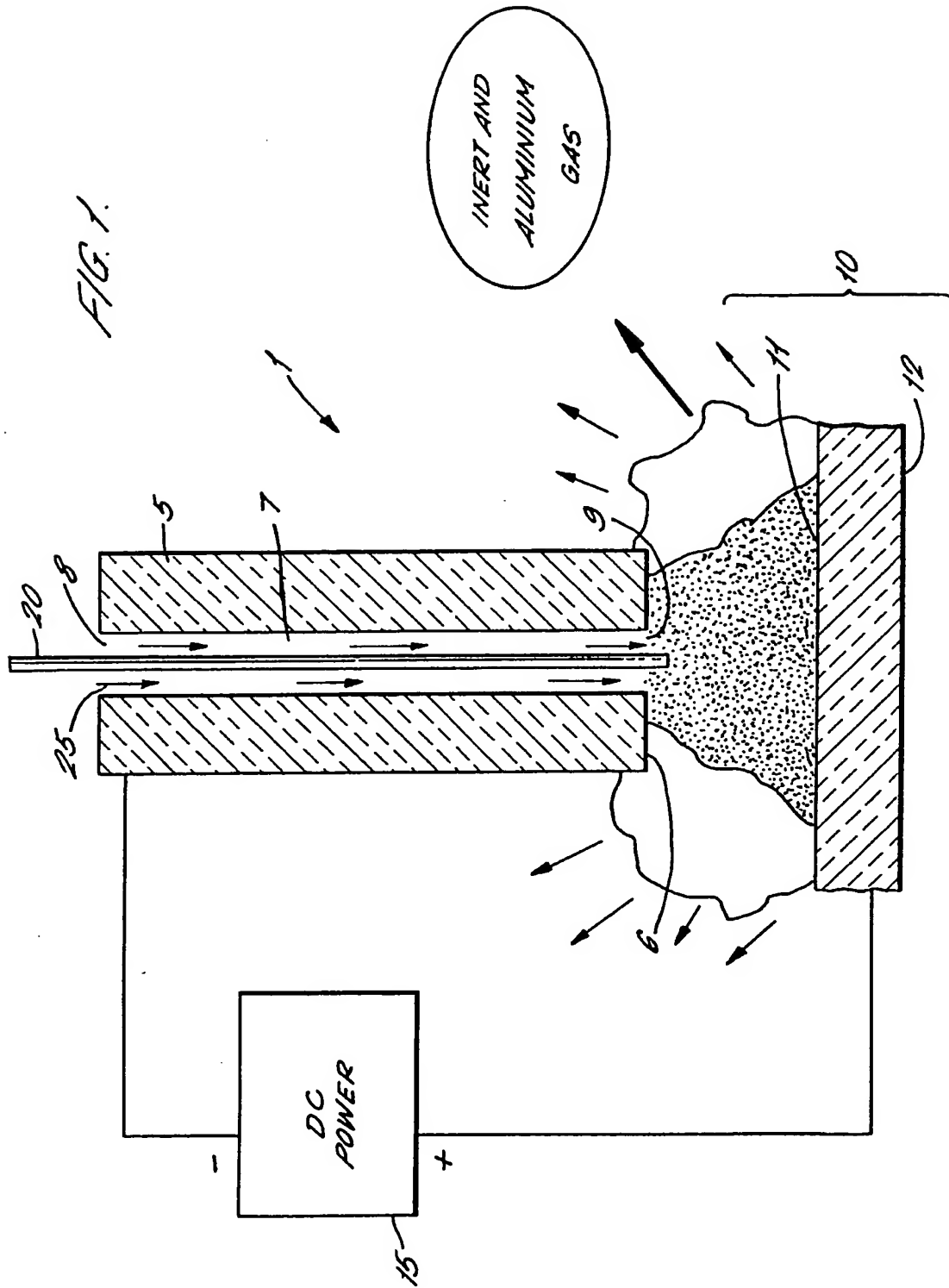
15           39. A particulate material as claimed in any one of claims 34 to 38, wherein the particles have a mono-crystalline core.

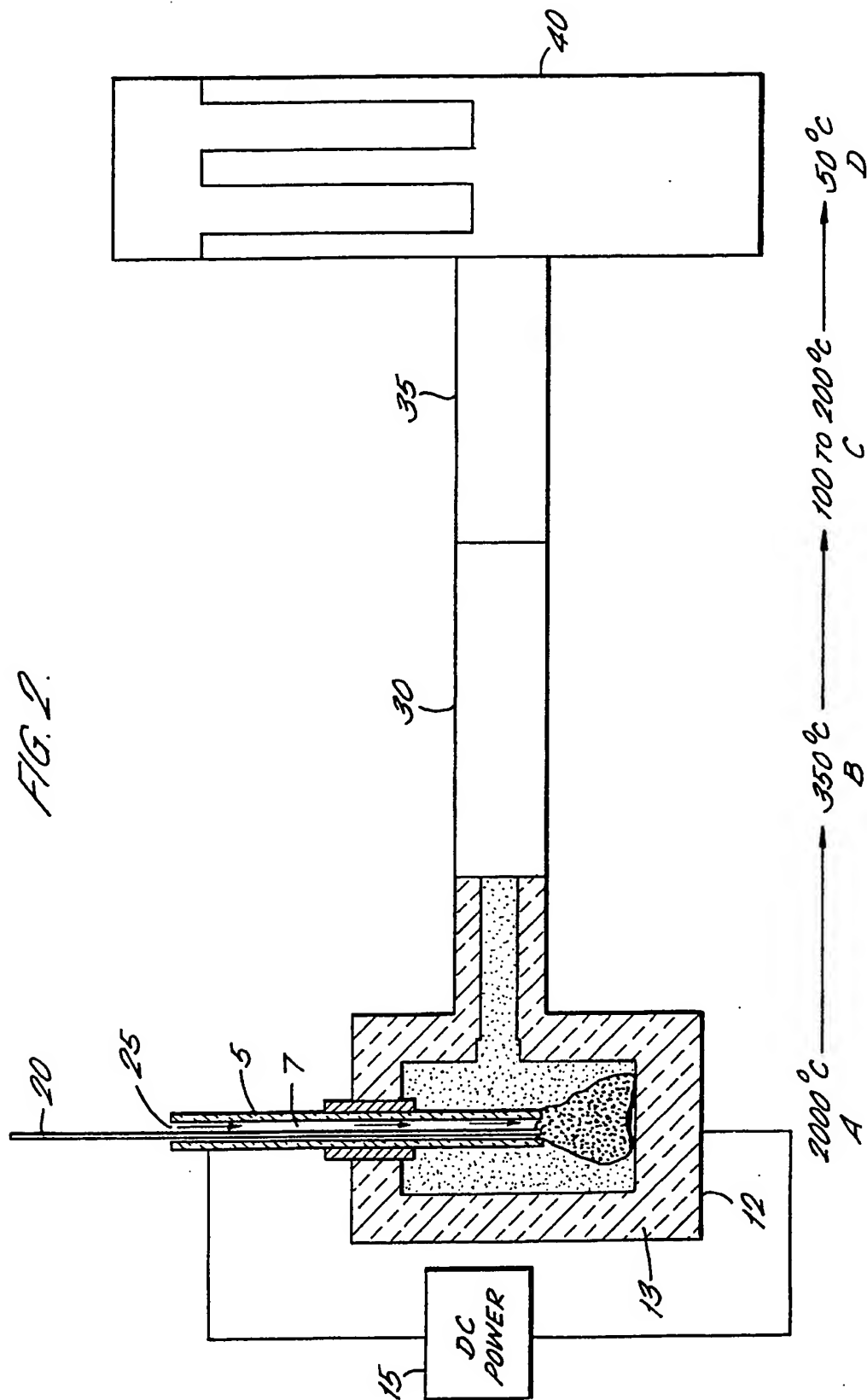
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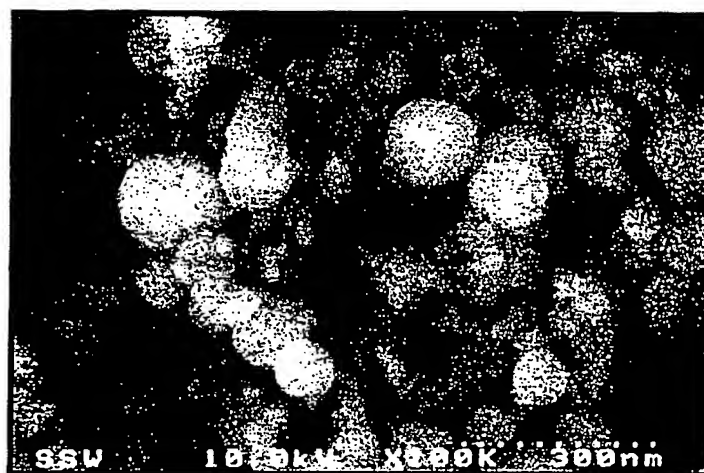
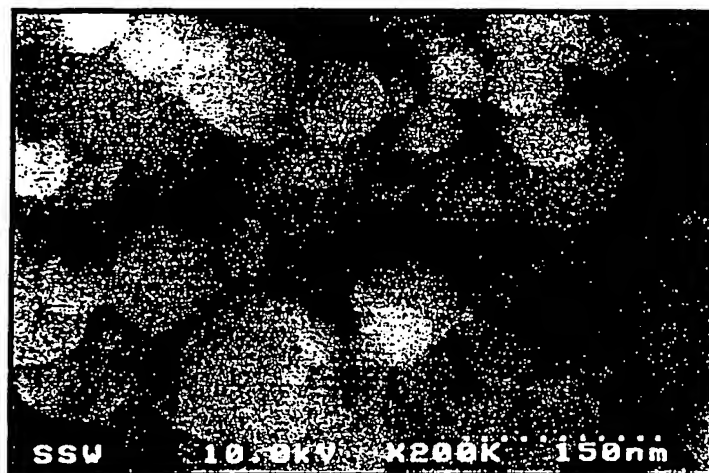
*FIG. 3.**(a)**(b)*

FIG. 4.

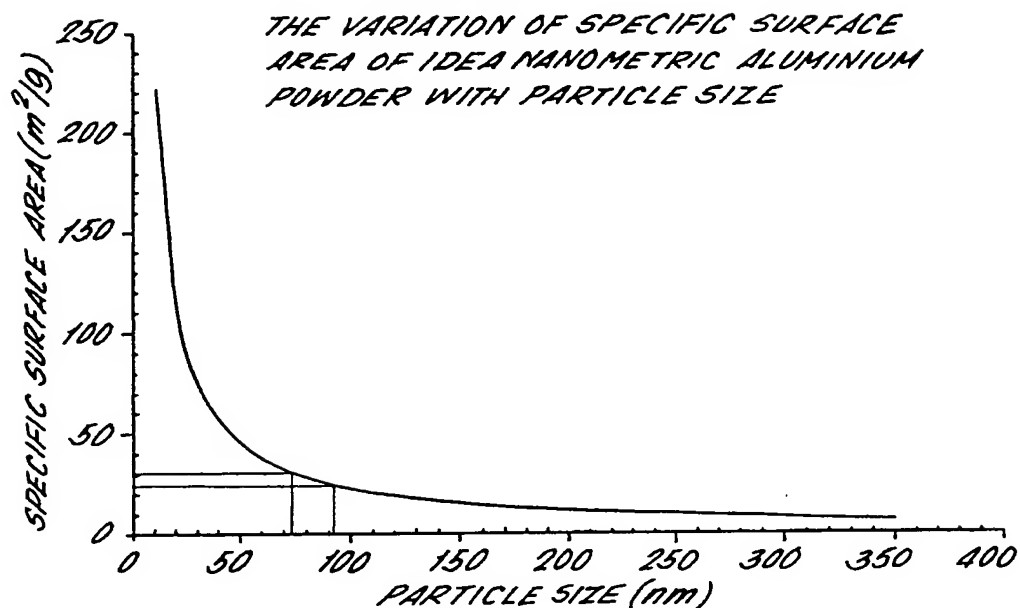


FIG. 5.

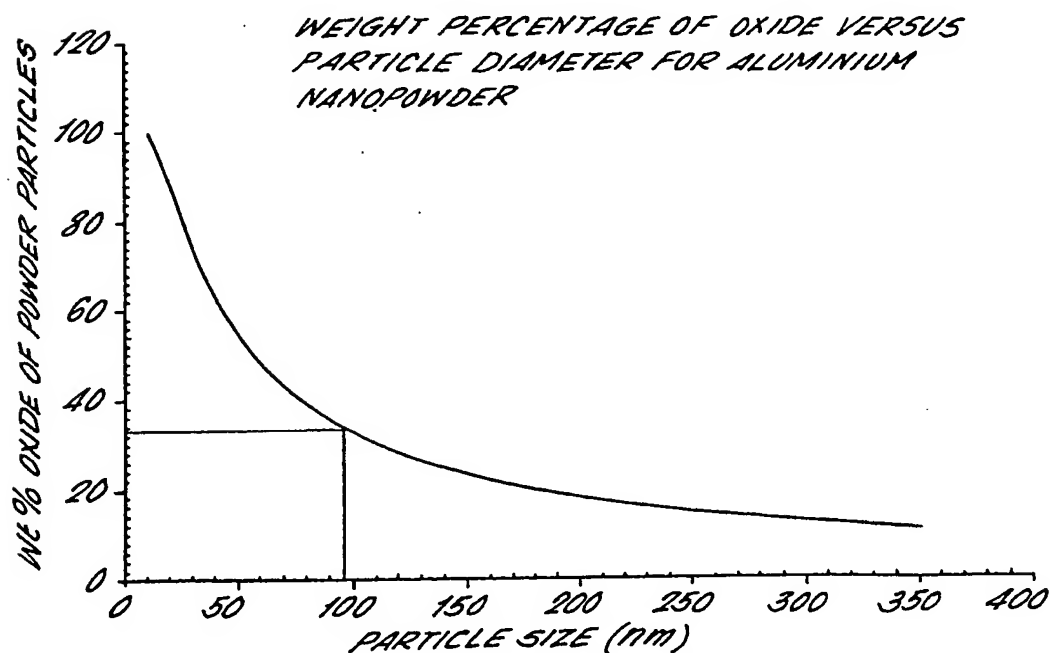


FIG. 6.

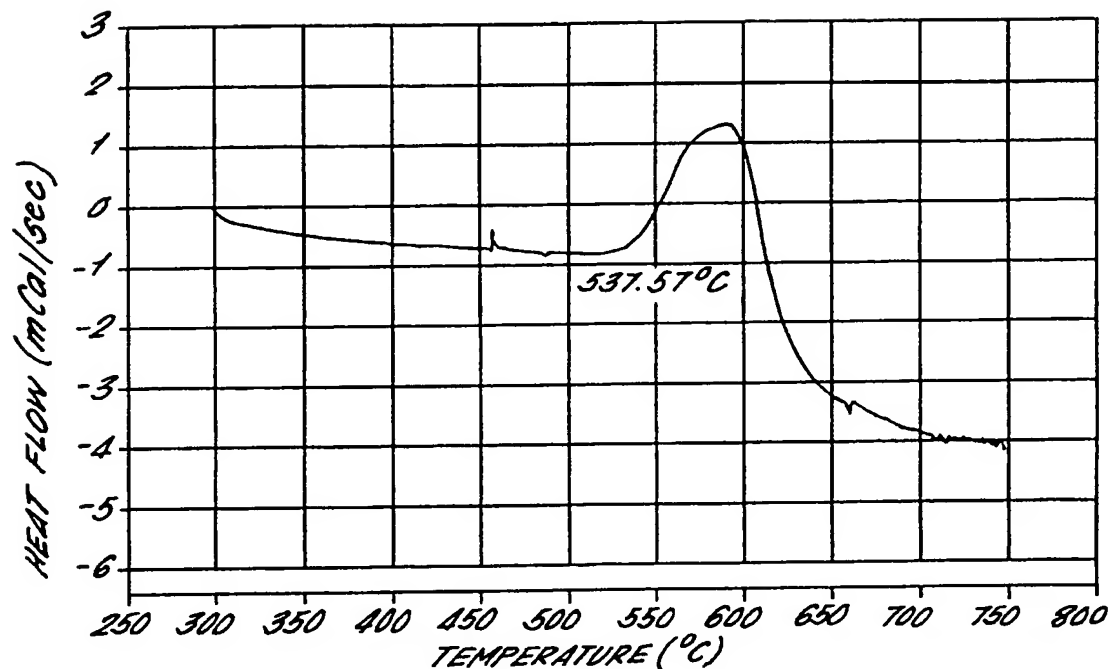


FIG. 7.

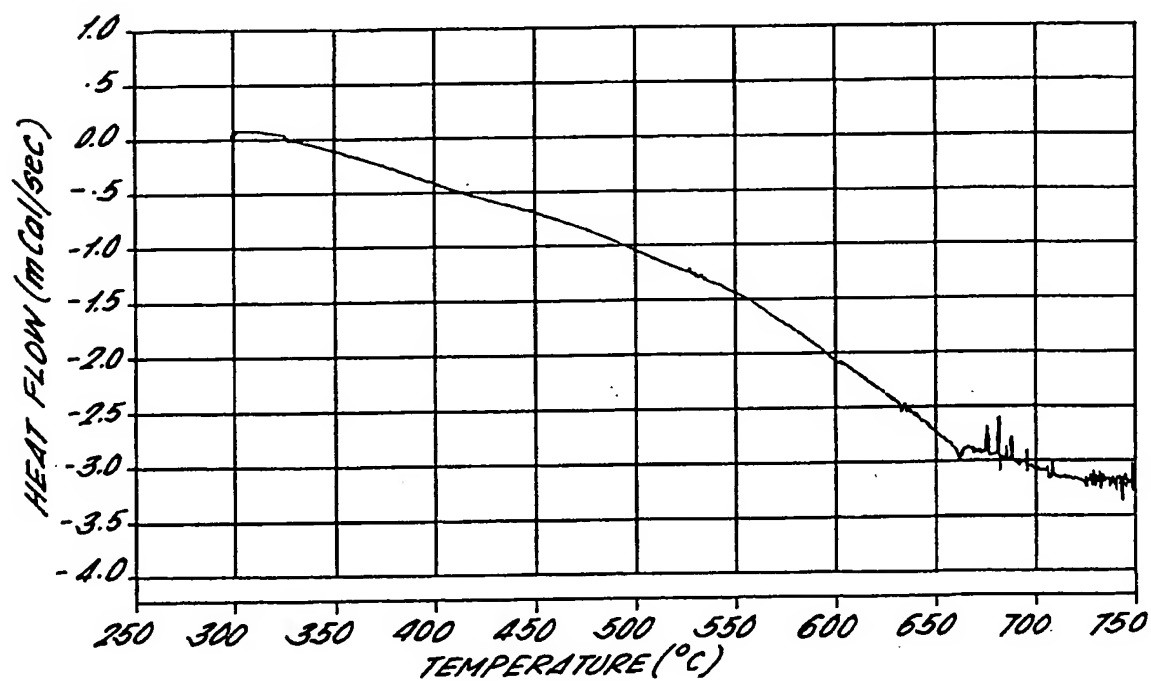
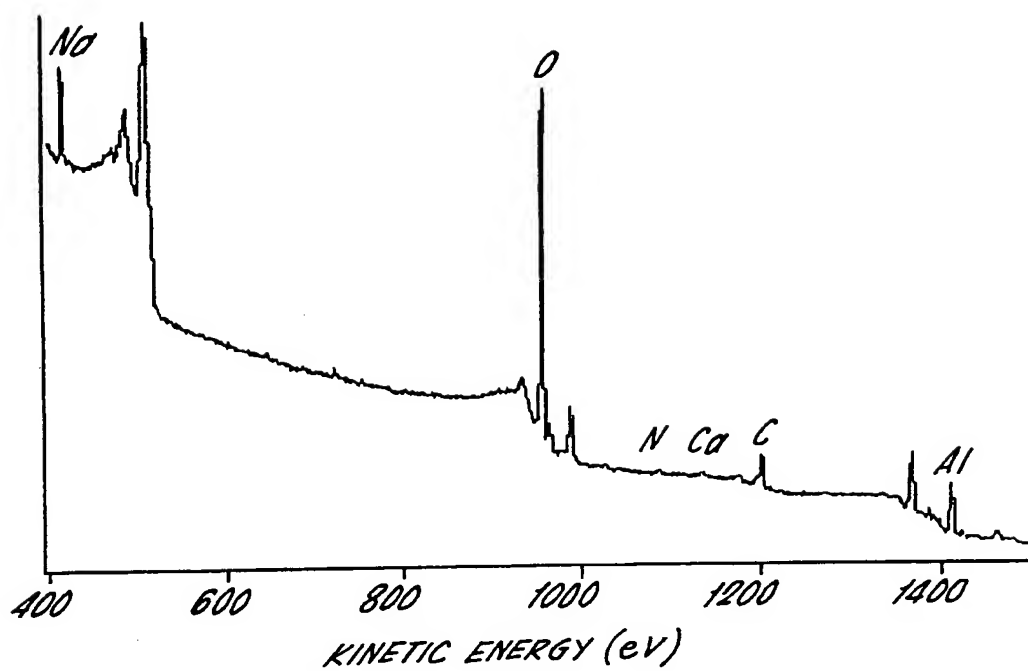


FIG. 8.





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/00553

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B22F9/12 H05H1/42

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B22F H05H C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 593 740 A (KUZNETSOV ANATOLY A ET AL) 14 January 1997 (1997-01-14)	1, 3, 5, 6, 8-11, 14-24
Y	column 2, line 45 -column 4, line 22	4, 25-39
Y	US 5 481 080 A (LYNUM STEINAR ET AL) 2 January 1996 (1996-01-02) column 3, line 34 -column 4, line 8	4
P, Y	US 6 146 505 A (GOTO MASAHIRO ET AL) 14 November 2000 (2000-11-14) column 5, line 5 -column 6, line 65	25-39
Y	& JP 10 256528 A 25 September 1998 (1998-09-25)	25-39

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Date of the actual completion of the international search

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Date of mailing of the international search report

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European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

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